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Calculating the Thermal Conductivity of Heterogeneous Systems

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Physical characteristics of composite materials have been investigated with increasing frequency in response to the rise in industry requirements for materials with specific properties. They include work on thermal and electrical conductivity of polymeric materials containing powders of different conducting fillers as the dispersed phase (Cullen et al., 1988; Holrook, 1988; Dinwiddie and Onn, 1989; Rule et al., 1990).

The conductivity of such composite materials has essentially a nonadditive characteristic depending to a great extent on the distribution of the filler particles in the matrix, that is, depending on the composition structure. In a real composite, single, isolated particles, complexes of associated particles, and chain structures may exist in some combinations (Gul and Shenphil, 1984).

The aim of this work is to show the construction of a model that offers the possibility to describe such systems, considering the particle fractions existing in three structural phases. Several theoretical models were suggested recently that determined the relation between microstructure and effective conductivity of filled composites (Beasley and Torquato, 1986; Smith and Torquato, 1989; Lu and Kim, 1990). However, simplified semitheoretical models, especially the Lewis and Nielson (Nielson, 1973) method including structural parameters, are used often by experimentalists (Hoffman et al., 1989) for predictions of thermal conductivity of composite materials. To describe their experimental data, Kusu and Cornelinssen (1975) suggested using the formula for the system of plates parallel to the flow with the introduction of an empirical coefficient. There seems to be no basis for using such a simplified model, which reflects inadequately the real, three-dimensional composite structure.

According to the studies of de Vriese (1955) and Rivkin (1989), the Bruggemann model (1935) proved to be better for the calculation of the thermal conductivity of filled polymers for isolated, uniformly-distributed inclusions, while that of Dul'nev (see Dul'nev and Novikov, 1977) was better for mutually-penetrating components. The models, however, describe only the conductivity of limiting structures without offering the possibility of going into intermediate variants.

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Description of the Model

Take the heterogeneous system, in which the particles may exist in three different phases: as isolated inclusions, in isolated aggregates of associated particles, and in chain structures (skeleton).

The relationship of phases is characterized by parameters α_s and α_a, which are defined by particle fractions in the skeleton and the aggregates, respectively. Thus, the volumetric fractions of the skeleton v_s and the aggregates v_a are the tightly packed systems of the filler particles expressed as follows:

$$v_s = \frac{\alpha_s v_2}{v_2^s}, \quad v_a = \frac{\alpha_a v_2}{v_2^a}$$

The heterogeneous system is considered a structure with mutually penetrating components: one the conducting skeleton and the other the medium, containing isolated particles and the aggregates. The thermal conductivity calculation of such a system is carried out in four stages.

1. The thermal conductivity calculation of skeleton λ_s and aggregates λ_a.

2. The effective thermal conductivity λ_M calculation of the polymer base with isolated inclusions (aggregates and skeleton are not taken into account).

3. The effective thermal conductivity $\bar{\lambda}_M$ calculation of the system of isolated aggregates in the medium with thermal conductivity λ_M.

4. The effective thermal conductivity calculation of the system with mutually-penetrating components λ, which is made up of the conducting skeleton and the medium with thermal conductivity $\bar{\lambda}_M$.

Figure 1 shows the order in which the structure's levels were considered when calculating the thermal conductivity of the system. The effective thermal conductivity of the aggregates λ_a and the skeleton λ_s, as well as that of systems containing the isolated inclusions λ_M and the isolated aggregates $\bar{\lambda}_M$ are given by the Bruggemann (1935) model:

$$\frac{\lambda_{II} - \lambda}{\lambda_{II} - \lambda_I}\left(\frac{\lambda_I}{\lambda}\right)^{1/3} = 1 - v_{II} \qquad (1)$$

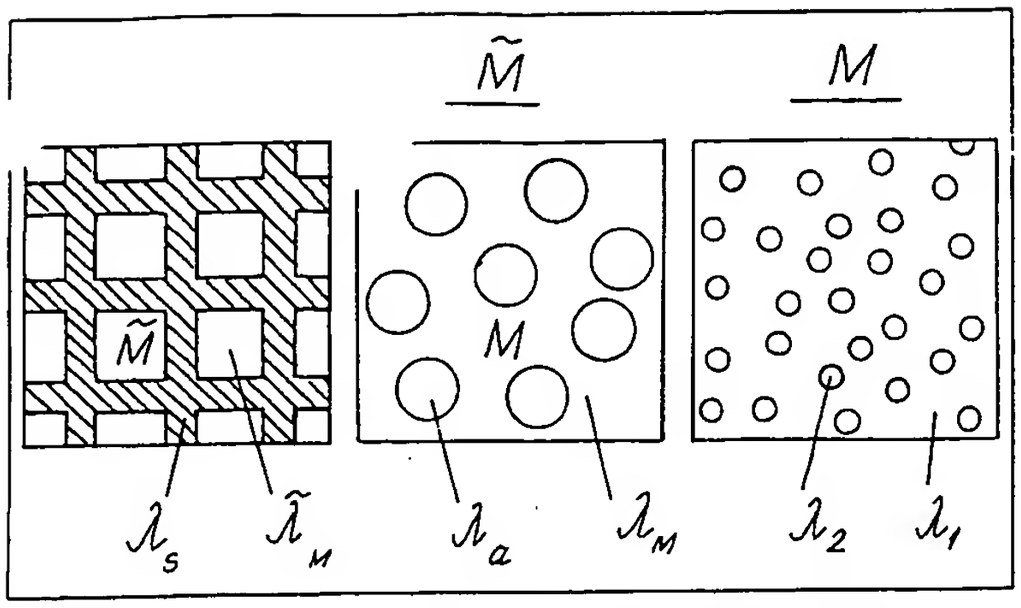

Figure 1. Order of levels of the structure.

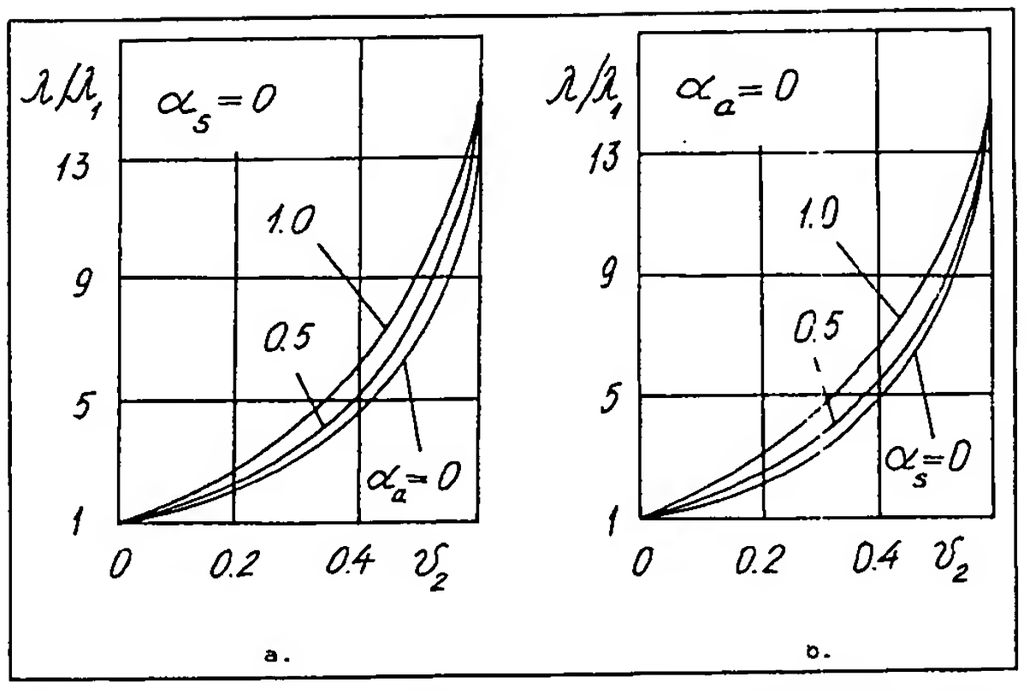

Figure 2. Calculated reduced thermal conductivity λ/λ_1 vs. filler concentration v_2 for composites.

They also include isolated inclusions, as well as (a) particle aggregates and (b) skeleton.

The choice of formula 1, which was recommended by de Vriese (1955) particularly for the thermal conductivity calculation of polymer systems containing isolated, evenly-distributed inclusions to high concentration, is based on the following.

1. In the extensive experimental study of Baranovsky (1970) where measures were incorporated to prevent the association of inclusions in the polymeric matrix, the data obtained for the composite thermal conductivity correlate well with the calculation according to formula 1 for different fillers.

2. Formula 1 was successfully applied by Pugatch and Rivkin (1988) for filled polymeric materials and for the calculation of thermal conductivity of the skeleton consisting of associated particles.

When calculating the aggregate thermal conductivity λ_a in the formula 1, the values were substituted:

$$\lambda_I = \lambda_1; \quad \lambda_{II} = \lambda_2; \quad v_{II} = v_2^a.$$

On calculating the thermal conductivity of the skeleton λ_s:

$$\lambda_I = \lambda_1; \quad \lambda_{II} = \lambda_2; \quad v_{II} = v_2^s.$$

The values of the particle concentration in the skeleton v_2^s and in the aggregates v_2^a depend on the density of their packing. In accordance with the recommendation by Rivkin (1989), the following values, $v_2^s = v_2^a = 0.6$, were used in calculation.

The effective thermal conductivity λ_M is calculated with:

$$\lambda_I = \lambda_1; \quad \lambda_{II} = \lambda_2; \quad v_{II} = (1 - \alpha_a - \alpha_s)\frac{v_2}{1 - v_s - v_a};$$

The effective thermal conductivity $\tilde{\lambda}_M$ is calculated with:

$$\lambda_I = \lambda_M; \quad \lambda_{II} = \lambda_a; \quad v_{II} = \frac{\alpha_a v_2}{v_2^a(1 - v_s)}.$$

At the fourth stage of calculation, the Dul'nev model is used for the system with mutually-penetrating components. The thermal conductivity of such a system is found by the formula:

$$\lambda = \lambda_s[c^2 + k(1-c)^2 + 2kc(1-c)\,(kc + 1 - c)^{-1}] \qquad (2)$$

where

$k = \tilde{\lambda}_M/\lambda_s$

$c =$ positive real root of $2c^3 - 3c^2 + 1 = u$

which can be determined by the formula:

$$c = 0.5 - \sin[1/3\text{arc}\,\sin(2u - 1)]$$

where

$u = 1 - v_s$

Figure 2 shows calculated dependencies of the reduced thermal conductivity of the composition λ/λ_1 on the filler concentration for the systems containing isolated aggregates (Figure 2a) and conducting skeleton (Figure 2b).

A rise in the reduced thermal conductivity with an increase in the structural parameters α results from the growing unevenness of the filler distribution. Indicated parameters in our model are in accordance with the two levels of the structure regularity: α_a corresponds to isolated aggregates (particle accumulations evenly distributed in the matrix); and α_s corresponds to the chain structures (particle accumulations unevenly distributed in the matrix as the skeleton).

In the two limiting cases of using such a model, the calculation leads to Bruggemann's formula ($\alpha_a = \alpha_s = 0$) with no filler structurization (fully-uniform system) and to the calculation according to Dul'nev's formula ($\alpha_a = 0$, $\alpha_s = 1$), where all the particles pass on to the conducting skeleton (a maximum uneven structure of the system).

When the average volumetric concentration of the filler in the composite approaches the particle concentration in the aggregates and the skeleton, the curves in Figures 2a and 2b corresponding to different α_a and α_s come nearer; and when $v_2 = v_2^a = v_2^s$, they are combined to one point. According to the model, such a composite is the tightly-packed system of the particles evenly-distributed in the matrix.

Discussion

In real composites, the content of the filler in any structural phase depends on many factors, especially on the technology of the composite preparation. The process of structurization and the degree of its completeness are affected by the viscosity of the mixture, the procedure of dispersion, and the regime of composite hardening. There are ways to regulate the dis-

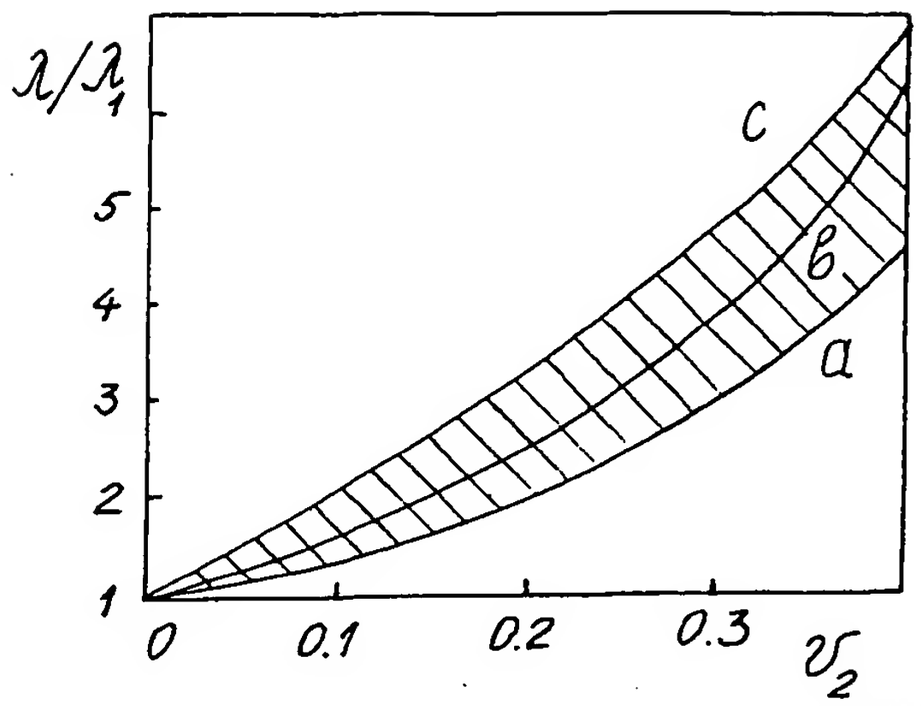

Figure 3. Reduced thermal conductivity of composites λ/λ_1 vs. filler concentration v_2, $\lambda_2/\lambda_1 = 500$, $v_2^a = v_2^s = 0.6$.

Calculation with following values of structural parameters; (a) $\alpha_a = \alpha_s = 0$; (b) $\alpha_a = 1$, $\alpha_s = 0$; and (c) $\alpha_a = 0$, $\alpha_s = 1$.

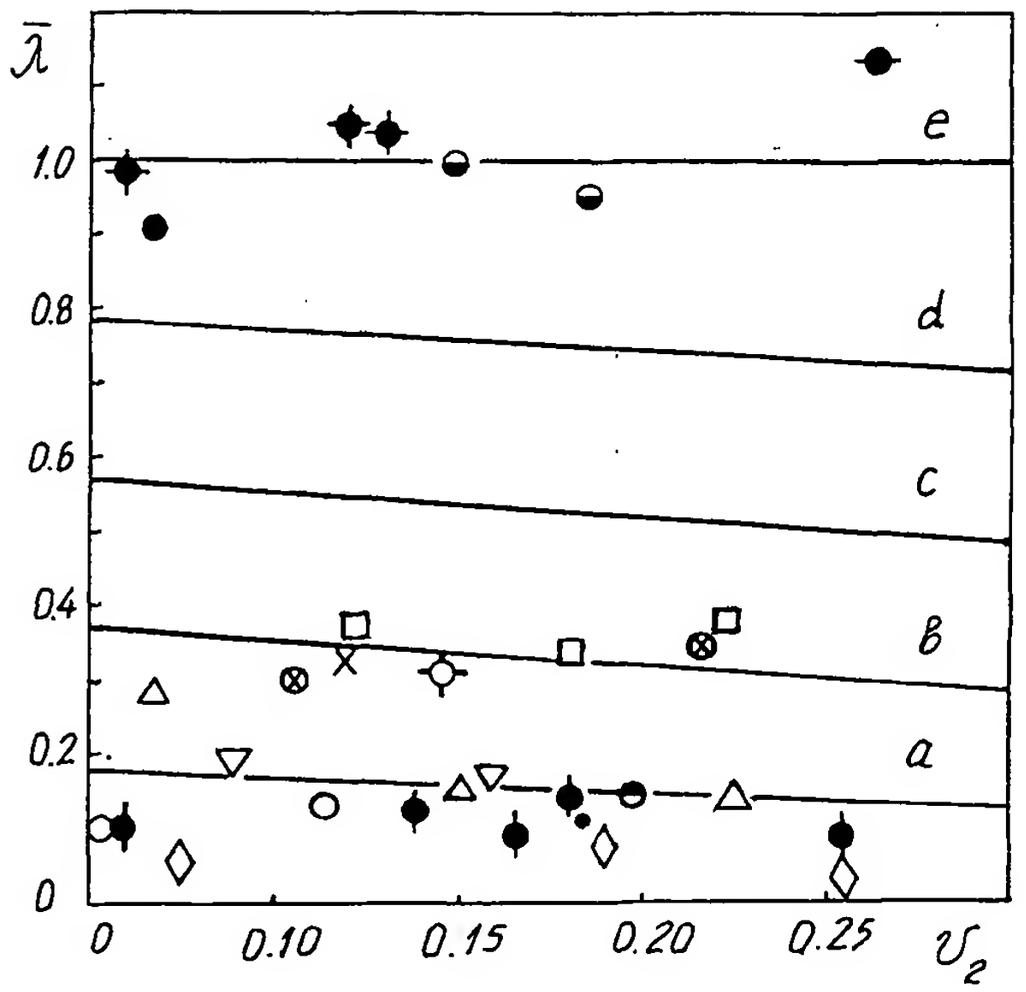

Figure 4. $\bar{\lambda}$ vs. v_2 for epoxy composites [6].

Curves a–e were calculated according to our model with the following values of α_s: (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8, and (e) 1, while $\alpha_a = 0$ (symbols as in Figure 5).

tribution characteristics of the filler particles, such as the pressing of the polymer and filler powders of different dispersivity, which results in the formation of the conducting skeleton at the borders of the polymer grains (Gul and Shenphil, 1984), the filling of powder coatings (Pugatch et al., 1988), and the introduction in the polymeric matrix of the substance preventing the particle association (Baranovsky, 1970).

In the case of composites obtained by the dispersion of the filler particles in a polymer melt, the character of the structurization depends on the relationship among interaction energies e_{11}, e_{12}, and e_{22}. Gul and Shenphil (1984) suggested an approach to predicting the structure that depends on the interaction energies. If the conditions $e_{11} > e_{12}$ and $e_{22} > e_{12}$ are fulfilled, a large number of aggregates are formed in composite which prevents formation of a continuous structure. If $e_{12} > e_{11}$ and $e_{12} > e_{22}$, the particles will be separated by considerable polymer layers and will not be inclined to associate. Conducting chain structures can be formed when on a part of the particle surface the conditions of $e_{12} > e_{11}$ are observed at the same time that there are sections on the surface for which the condition $e_{22} > e_{12}$ is true.

With real composites where there are, as a rule, different relations to the interaction energies, the structural modifications mentioned previously can exist in some combinations. In most cases, when it is impossible to determine the structure of the filler distribution in the composite, that is, when α_a and α_s are unknown, we can point out the region of possible values of thermal conductivity. Such a region is shaded in Figure 3 for the relation of the filler and the matrix thermal conductivities $\lambda_2/\lambda_1 = 500$. Curve *a* in this diagram corresponds to the uniform distribution of the filler $\alpha_a = \alpha_s = 0$. Curve *c* corresponds to the limiting, uneven distribution of the filler $\alpha_a = 0$ and $\alpha_s = 1$. Curve *b* corresponds to the location of the filler in isolated aggregates $\alpha_a = 1$ and $\alpha_s = 0$, and takes an intermediate position.

For a description of concrete experimental data, we take $\alpha_s = \alpha$ and $\alpha_a = 0$. In this case, the location of the composition in the indicated region is determined by the volumetric concentration of the filler v_2 and the parameter α. In this case, the parameter α characterizes irregularity of the filler location or the degree of structurization without any difference in which the structural phase the filler is present. To divide clearly the compositions into degrees of structurization, it is convenient to pass on to dimensionless thermal conductivity:

$$\bar{\lambda} \equiv \frac{\lambda - \lambda'}{\lambda'' - \lambda'} \tag{3}$$

where

λ' = thermal conductivity of the uniform system calculated according to our model with the parameters $\alpha_a = \alpha_s = 0$

λ'' = thermal conductivity of the limiting, uneven system where the whole of the filler is located in the conducting skeleton ($\alpha_a = 0$, $\alpha_s = 1$)

In the calculation we assume that the parameter α does not depend on the concentration of the filler and is constant for the given composition. This means that an increase in filler content in the polymeric matrix does not affect the character of the structurization. When α is constant there are no percolation effects, which is confirmed by experimental data for filled polymers and can be explained by the presence of a polymer film between the particles.

Figure 4 shows the grid of $\bar{\lambda}$, v_2 calculated behavior as well as experimental data obtained by Rivkin (1989) for epoxy composites. Such data representation made it possible to classify studied fillers in terms of structural parameter α. The results are shown in Table 1. Presented values of α can be used in the first approximation for the calculation of thermal conductivity of the polymeric composites obtained by means of dispersion in a melt. The experimental thermal conductivity data (Rivkin, 1989) and the results calculated with our model are shown in Figure 5 in terms of λ/λ_1 and v_2. According to Fig. 5 and Table 1, it is quite obvious that deviation of the experimental data from the model calculations are within 5–

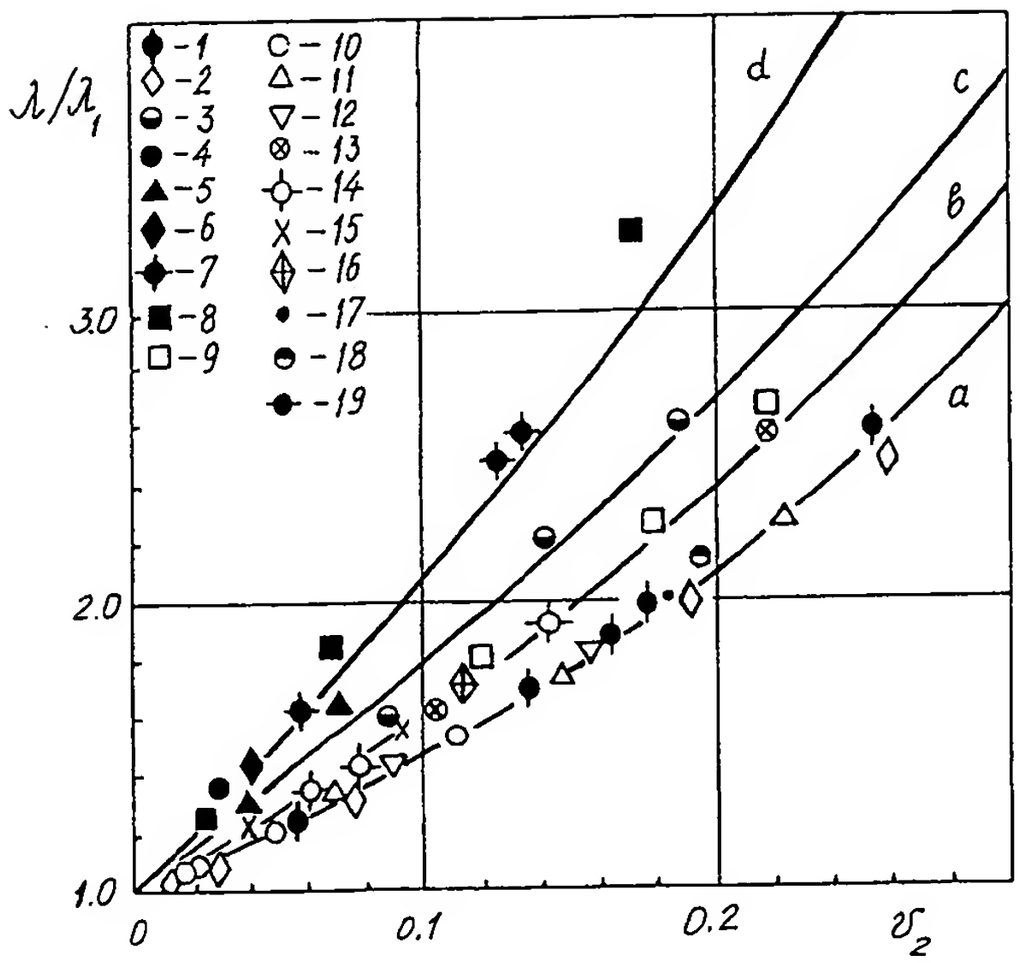

Figure 5. Reduced thermal conductivity of epoxy composites λ/λ_1 as a function of filler concentration v_2 ($T = 350$ K).

(1) Al
(2) Zn
(3) Ti
(4) W
(5) Ni
(6) bronze flakes
(7) aluminum flakes
(8) colloidal graphite
(9) graphite (30–50 μm)
(10) Cr_2O_3
(11) Al_2O_3 #1 (20–30)
(12) Al_2O_3 #2 (0.5–1)
(13) Si_3N_4
(14) AlN #1 (1–10)
(15) AlN #2 (0.01–0.1)
(16) AlN (70% #1 + 30% #2)
(17) B_4C
(18) SiC
(19) ZnO

Curves were calculated according to our model with $\lambda_1 = 0.22$ (W/m·K) and the following:
(a) $\lambda_2 = 36$ W/(m·K), $\alpha_a = 0$, $\alpha_s = 0.2$
(b) $\lambda_2 = 100$ W/(m·K), $\alpha_a = 0$, $\alpha_s = 0.4$
(c) $\lambda_2 = 17$ W/(m·K), $\alpha_a = 0$, $\alpha_s = 1.0$
(d) $\lambda_2 = 150$ W/(m·K), $\alpha_a = 0$, $\alpha_s = 1.0$

10%, that is, it does not exceed experimental errors. For brevity, analytical predictions of our model will not be compared with extensive experimental data acquired in other works.

As soon as parameter α characterizes the structure of the composite, it can be used to predict some properties connected with the structure. It is also possible in some cases to solve the reverse problem.

Table 1. Fillers Classified in Terms of Structural Parameter

Fillers	Value of Structural Parameter α	Maximum Deviation $\left\lvert\frac{\lambda_e - \lambda_c}{\lambda_e}\right\rvert_{MAX}$
ZnO, C (Colloidal Graphite), W, Ni, Ti, Aluminum and Bronze Flakes	1	0.10
Al_2O_3, Cr_2O_3, Al, Zn, B_4C, SiC	0.2	0.05
Si_3N_4, AlN of Different Dispersivities, C (30–50 μm)	0.4	0.05

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Notation

c, k, u = dimensionless parameters
e_{11} = interaction energy of polymer macromolecules
e_{12} = interaction energy of polymer and filler particles
e_{22} = interaction energy of filler particles
v_{11} = volumetric concentration of considered inclusions (particles or aggregates)
v_2 = volumetric concentration of filler particles
v_2^a, v_2^s = particle concentrations in aggregate and skeleton
v_a, v_s = volumetric fractions of aggregates and skeleton in the composite

Greek letters

α = structural parameter
α_a, α_s = particle fractions in aggregates and skeleton
λ = effective thermal conductivity of composite
λ_1 = thermal conductivity of considered matrix
λ_{11} = thermal conductivity of considered inclusions
λ_1, λ_2 = thermal conductivities of continuous phase (polymer) and filler particles
λ_a, λ_s = effective thermal conductivities of aggregates and skeleton
λ_c, λ_e = calculated and experimental thermal conductivities of composites
λ_M = effective thermal conductivity of the polymer base with isolated inclusions
$\tilde{\lambda}_M$ = effective thermal conductivity of the system of isolated aggregates in the medium with thermal conductivity λ_M
λ' = calculated value of λ with $\alpha_a = \alpha_s = 0$
λ'' = calculated value of λ with $\alpha_a = 0$, $\alpha_s = 1$
$\bar{\lambda}$ = dimensionless thermal conductivity defined by Eq. 3

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